Ion conductive high Li^+ transference number polymer composites for solid-state batteries

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Lawrence Berkeley National Laboratory

June 21-25, 2022

Project ID: bat538

Overview

Timeline

- Start Date: Oct. 1, 2021
- End Date: Sept. 30, 2026
- Percent complete: 5%

Budget

- Total budget (5 years): $1385K
- FY22 funding: $275K

Partners/Collaborators

Kristin Persson (UCB/LBNL), for molecular dynamics studies

Nitash Balsara (UCB/LBNL), for electrochemical characterization of transport properties

Barriers Addressed

- Energy Density
- Safety
- Low rate capability

*note: accomplishments will be primarily from prior project, "Designing high lithium-ion transference number and highly stable electrolytes for lithium metal batteries."

Relevance

- Solid state electrolytes could improve safety of Li metal batteries compared to organic liquid electrolytes by suppressing dendrite growth and eliminating flammable battery components.
- Thin film ceramic electrolytes have excellent conductivity, but suffer from being brittle, which limits their processability, particularly at the thicknesses necessary to compete against current state-of-the-art batteries.
- Engineering a porous cathode with ceramic ion conductors has proven challenging due to large solid-solid contact resistances.
- Polymer electrolytes suffer from very poor conductivity, but good processability
- We aim to combine the processability of polymers with the high conductivity of ceramics. We also will focus on engineering the cathode-composite electrolyte interface.

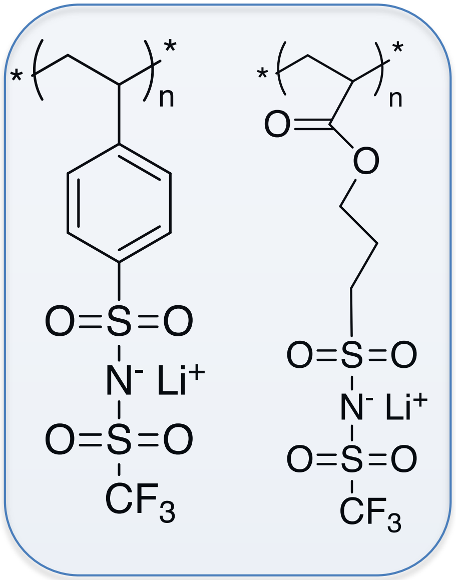
Objectives for FY22

- Develop the polymer chemistry to use in the polymer-inorganic composite electrolyte.
- Characterize electrochemical transport and interfacial properties of neat polymers in Li-Li symmetric cells.
- Optimize protocol to create thin films of inorganic-polymer mixtures.

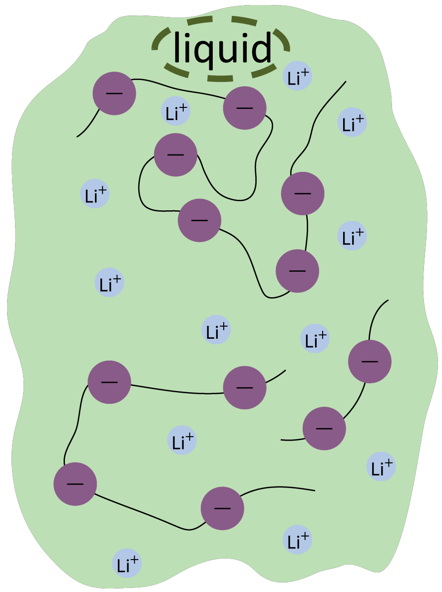
Milestones

Date	Milestones	Status
December 2021	Establish polymer synthesis by making two neat TFSI-containing polymers.	Completed
March 2022	Measure conductivity of two polymers using Li-Li symmetric cells	Completed
June 2022	Measure interfacial impedance evolution of polymer in a Li-Li cell.	On track
September 2022	Synthesize a series of four copolymers with various ratios of TFSI monomer and a film-forming monomer.	On track

Approach*

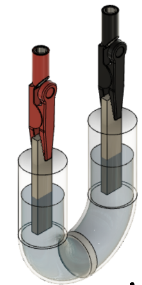


Synthesis

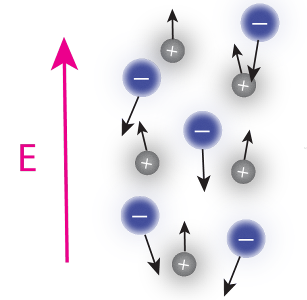


Preparation

Characterization



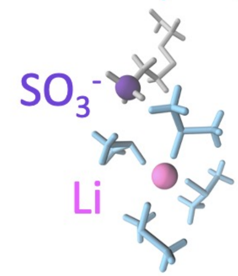
Concentration cell



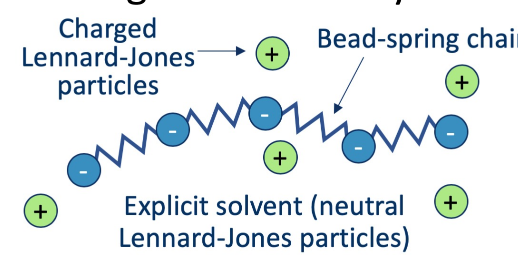
Electrophoretic migration net displacement

Modeling (w/ K. Persson)

Solvent-Separated Ion Pair (SSIP)



Coarse grained mol. dynamics



- Focus in 2021: Develop electrophoretic nuclear magnetic resonance (eNMR) as a tool to reduce error in electrochemical transport measurements.
- Focus in 2021: Synthesize single ion-conducting polymers with low molecular weight.
- Use molecular dynamics to understand molecular underpinnings of ion transport trends

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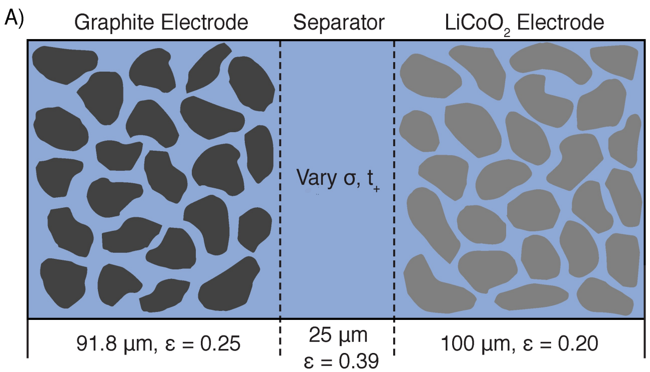
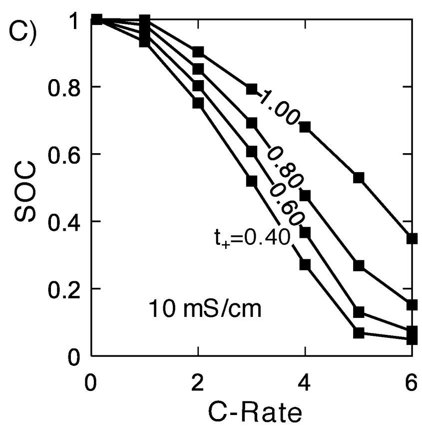
*Approach is from prior project that ended in Sept. 2021. Please see future work for proposed approach and plan for current project

Background: Motivation to study polyelectrolyte solutions

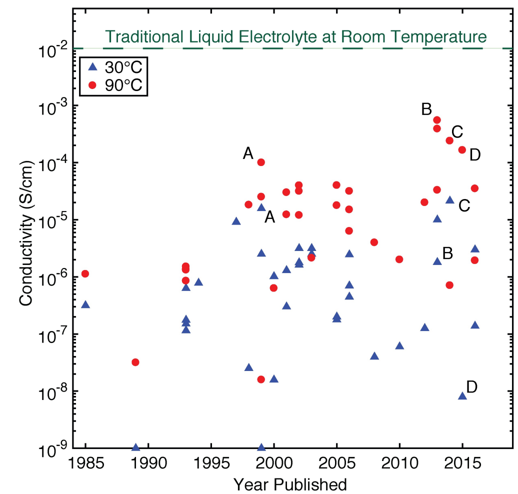
- Newman-type modeling predicts high transference number electrolytes would enable higher C-rates in Li-ion batteries

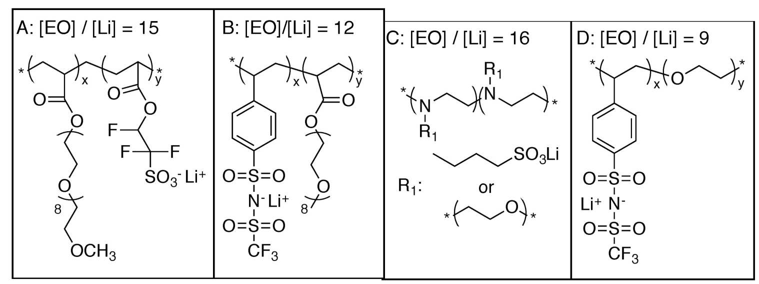


$$t_+ = \frac{D_+}{D_+ + D_-}$$



- Dry polymer electrolytes suffer from low conductivity (each point is a unique polymer)





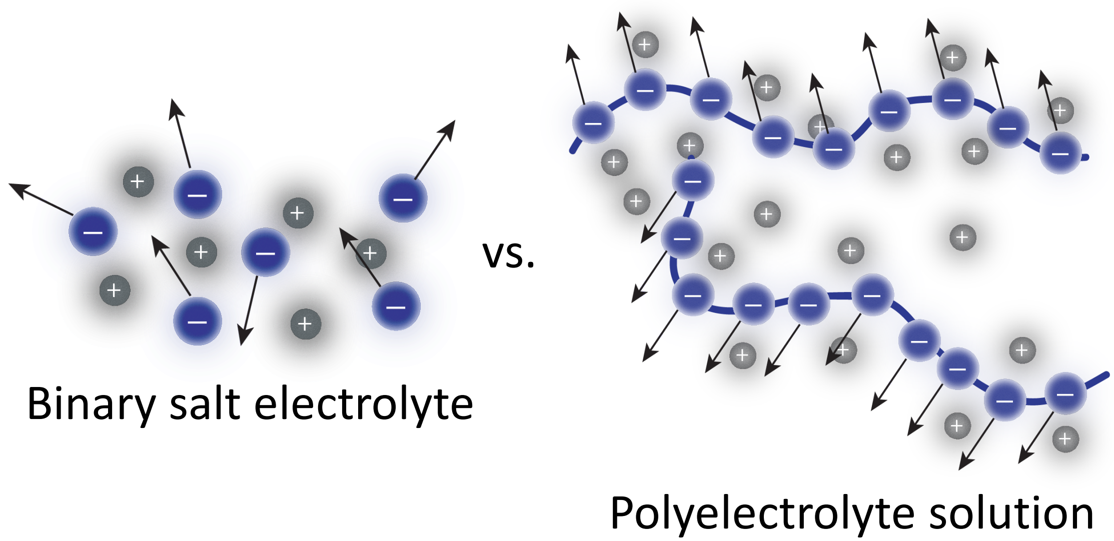
Systematically understand enhancements in transport by adding solvent

Diederichsen; McShane; McCloskey. *ACS Energy Lett.* 2017, *2*, 2563-2575.

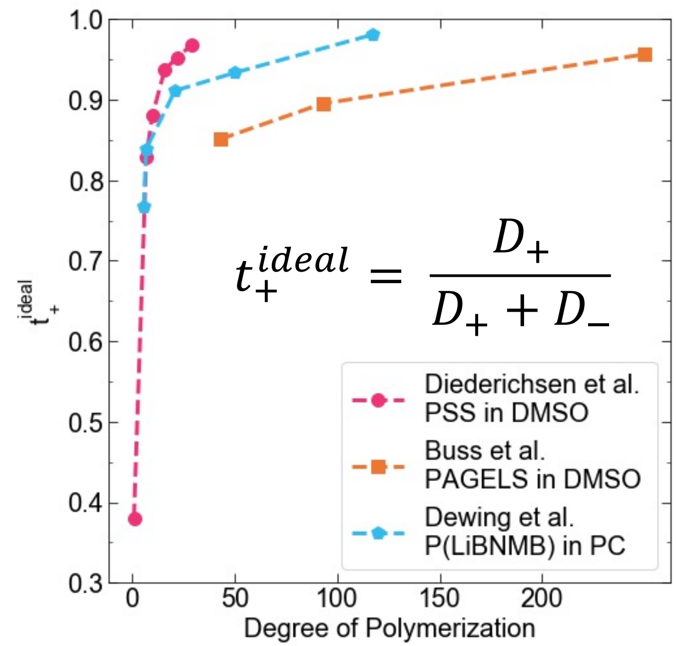
Background: Polyelectrolyte solutions potentially have high transference number and conductivity

Anion tethered to a polymer backbone then dissolved in a battery compatible solvent

- Slower anion diffusion compared to binary salt
- Greater charge on anion
- Conductivities ~1 mS/cm at room temp.



Transference number of various polyelectrolytes measured using pulsed NMR techniques assuming no ion correlations exist (ideal behavior)



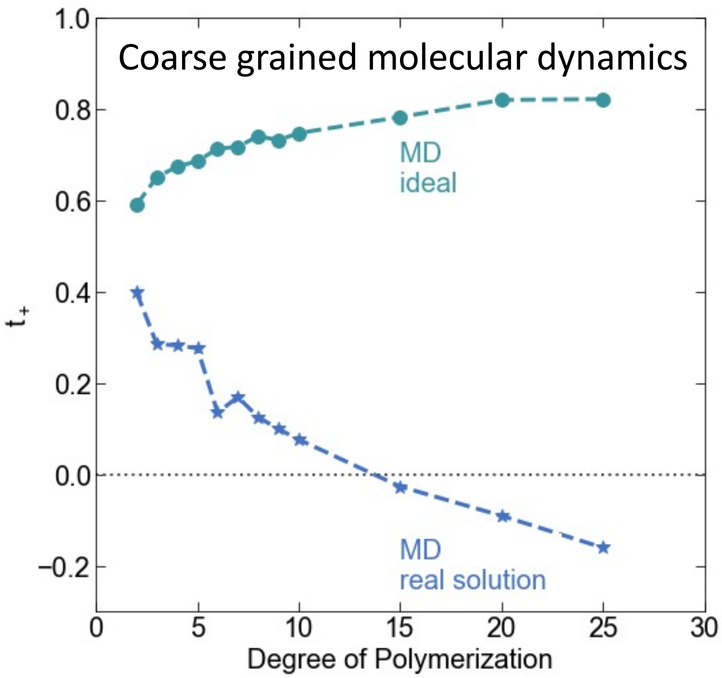
Accomplishment: Simulations predict low t^+ for polyelectrolyte solutions when accounting for ion correlations

$$c_i(\boldsymbol{v}_i - \boldsymbol{v}) = -\sum_j L^{ij} \nabla \overline{\mu}_j \rightarrow L^{ij} = \frac{V}{3k_B T} \int_0^\infty dt \langle \boldsymbol{J}_i(t) \cdot \boldsymbol{J}_j(0) \rangle \rightarrow t_i = \frac{F z_i c_i u_i}{\kappa} = \frac{\sum_j L^{ij} z_i z_j}{\sum_k \sum_l L^{kl} z_k z_l}$$

Onsager transport equations

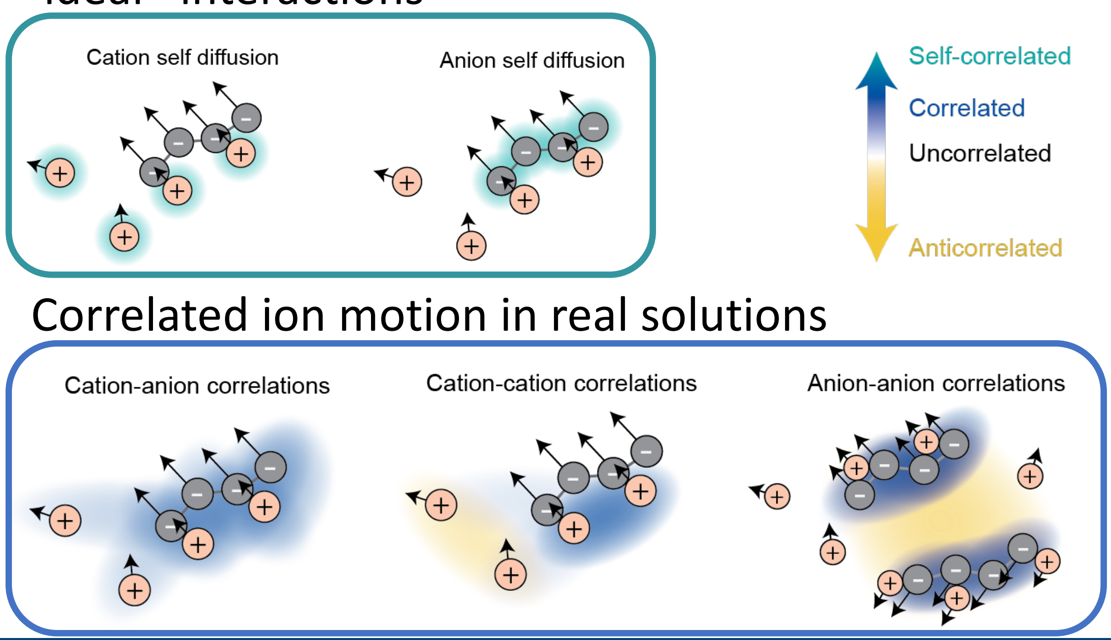
Green-Kubo relations for L^{ij}
Computed from molecular dynamics (MD)

Transference number



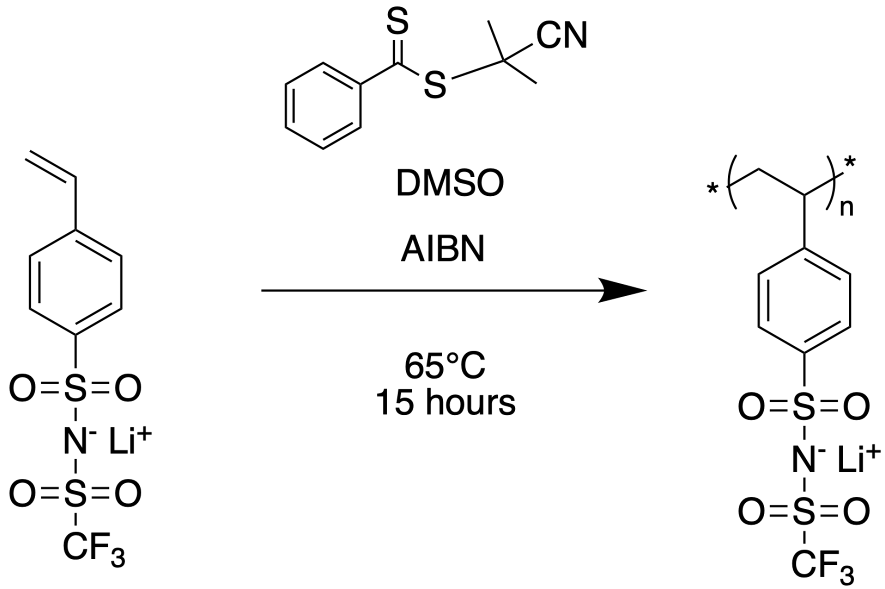
'ideal' interactions

Correlated ion motion in real solutions



How do we accurately measure polyelectrolyte solution t_+ experimentally?

Accomplishment: model polyanion synthesis using reversible addition-fragmentation chain transfer (RAFT) polymerization



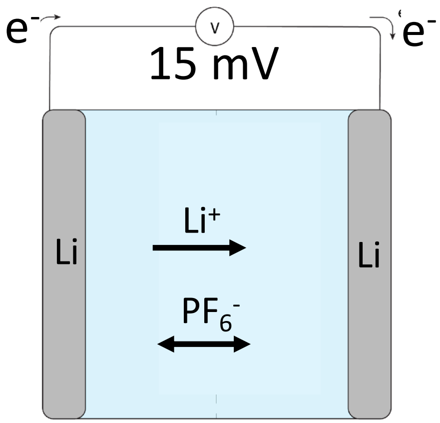
Poly(styrene-trifluoromethyl sulfonyl imide) (PS-LiTFSI)

Soluble up to 1-2M Li^+ in 3:7 EC:EMC

Repeat units	M_n (g/mol)	PDI
1	321	–
10	3,200	1.07
20	6,400	1.09
40	12,800	1.31

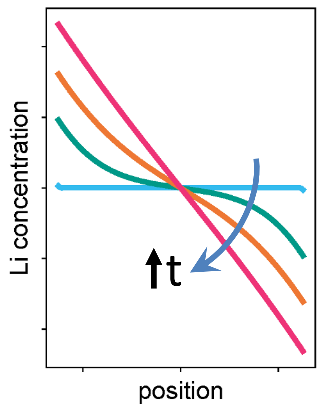
Small chain polymers prepared with good polydispersity and yield

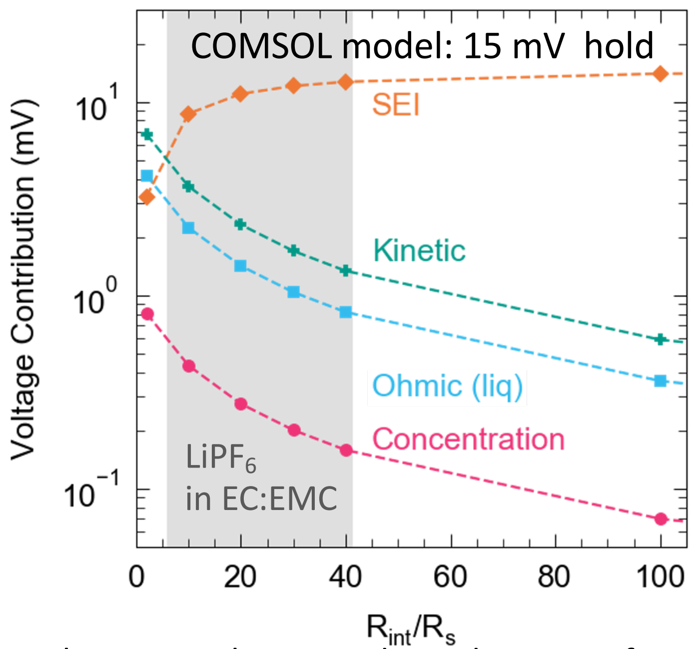
Previous Accomplishments: Voltage loss contributions across a polarized Li-Li cell

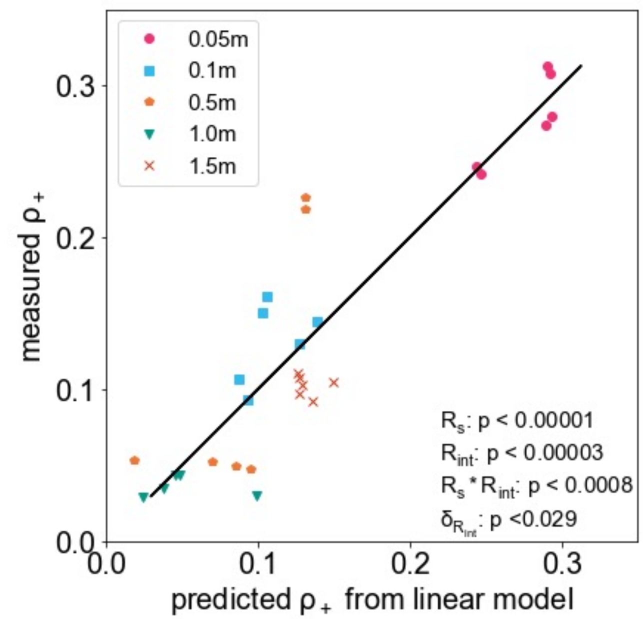


- SEI resistances dominate potential drop in liquid electrolytes during potentiostatic polarization
- Measured current ratio (ρ_+) can be predicted from a linear statistical effects screening model using interfacial resistance (Rint), its standard deviation (δ_{Rint}), and electrolyte Ohmic resistance (R_s)
- ρ_+ should only depend on i_{ss} and R_s

$$\rho_+^{\text{expt}} = aR_s + bR_{\text{int}} + c\delta_{R_{\text{int}}} + dR_sR_{\text{int}}$$







Ohmic contribution is desired quantity for ρ_+ calc.

$$\frac{I_{ss}/\Delta\phi_{ss}}{I_\Omega/\Delta\phi_0} = \frac{I_{ss}(\Delta V - I_\Omega R_0)}{I_\Omega(\Delta V - I_{ss}R_{ss})} = t_+^{id} = \rho_+$$

For a 15 mV hold, Ohmic contribution only accounts for ~1 mV, SEI dominates. Polarization measurements involving high interfacial impedance, low electrolyte resistance result in experimental artefacts that make deconvolution of both difficult

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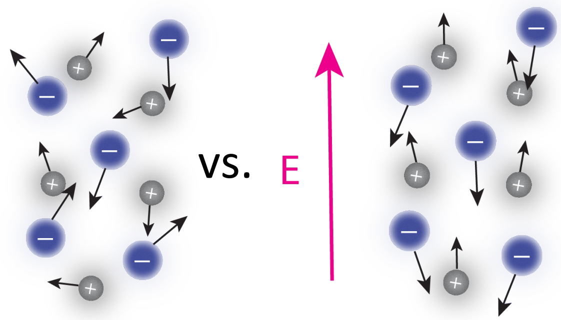
Accomplishment: establish electrophoretic NMR (eNMR) to measure ion velocities through electric field

- drift of ions in electric field manifests as a phase shift in NMR signal



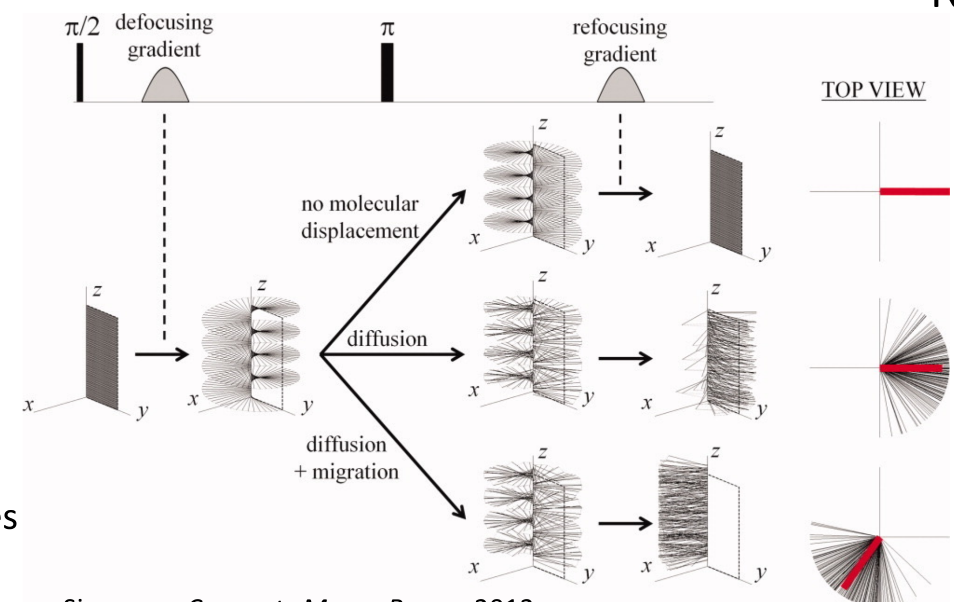
Brownian motion
no net displacement

Pulsed (PFG) NMR
-measures only self-diffusion (ideal)

Electrophoretic migration
net displacement

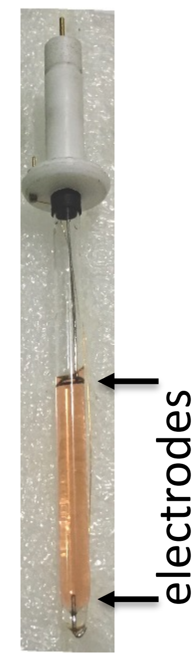
eNMR
-measures ion velocities (u_i) in electric field

$$t_i = \frac{F z_i c_i u_i}{\kappa}$$

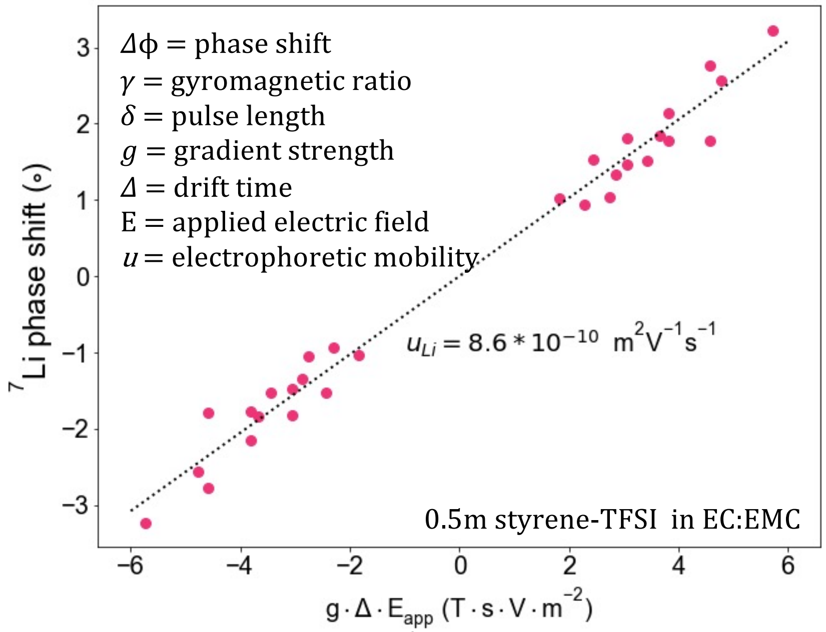


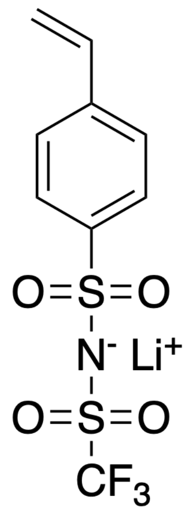
Sinnaeve. *Concepts Magn. Reson.* 2012
Fang, Yushmanov, & Furo . *J. Magn*. Reson. 2020

NMR tube

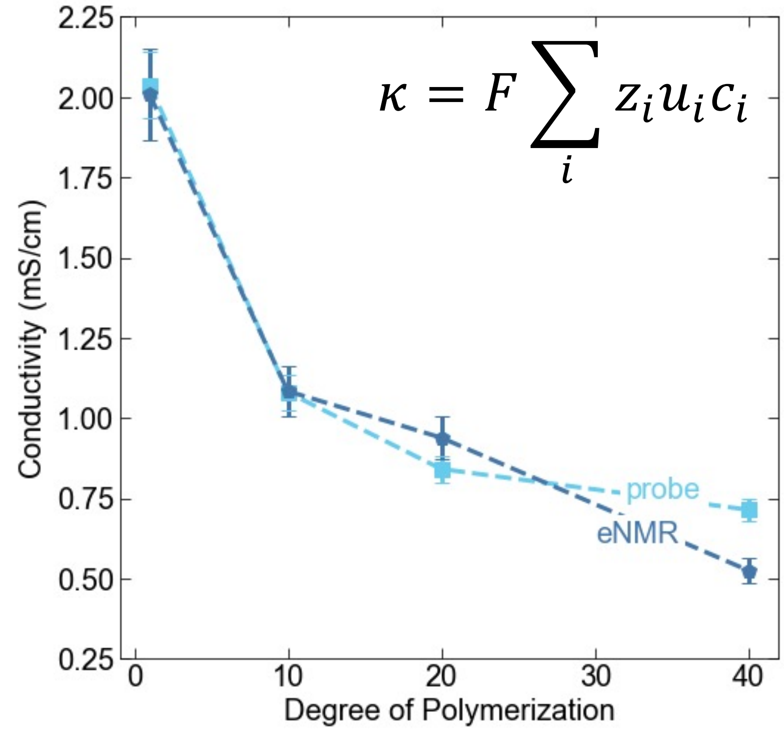


Accomplishment: establish electrophoretic NMR (eNMR) to measure ion velocities through electric field (II)





styrene-TFSI



phase shift, pulse length, drift time

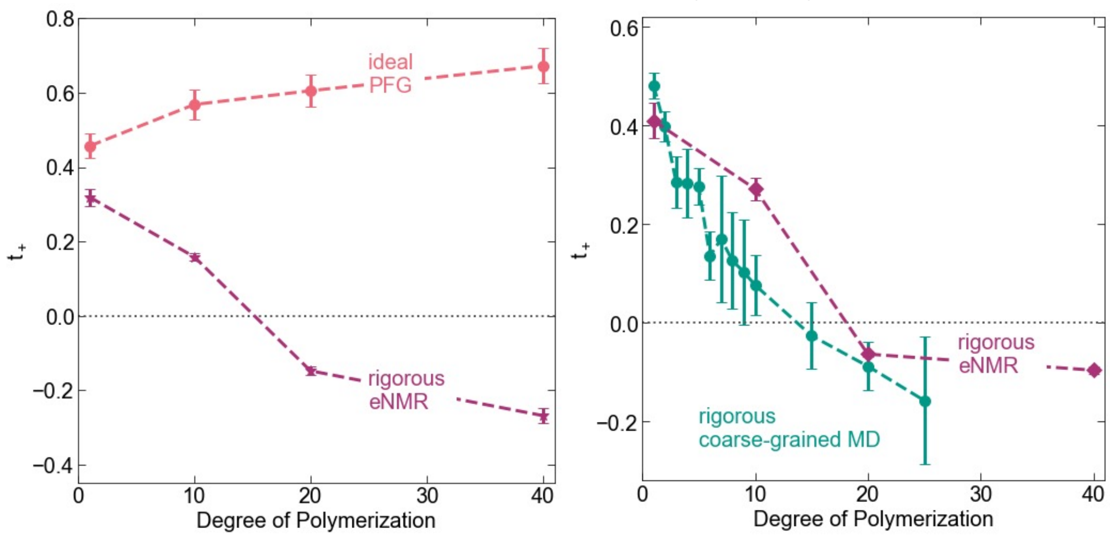
$$\Delta\Phi = \gamma_i \delta g \Delta E_{dc}\ u_i$$

gyromagnetic ratio, gradient strength, Electric field, Ion mobility

eNMR provides excellent agreement with conductivity probe measurement

Accomplishment: t^+ measurement using pulsed field gradient (PFG) NMR and eNMR

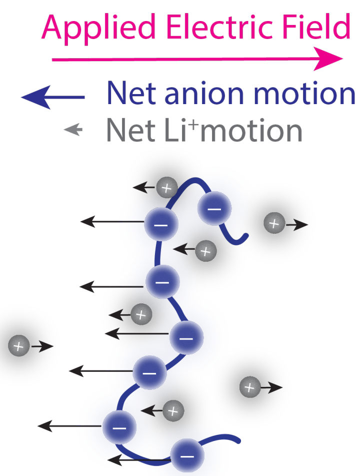
0.5m PS-LiTFSI in 3:7 EC:EMC (wt.%)



When ion velocities are measured using eNMR, rather than self-diffusion coefficients using PFG-NMR, t^+ decreases with increase mol. weight, reaches negative values

As MW increases

- anion self diffusion decreases but not as much as intra-chain anion-anion correlated motion increases
- cations bound to same chain are highly correlated
- cation-anion pairs can have long residence times



negative t_+ suggests significant fraction of negatively charged ion clusters

Accomplishment: Publications and presentations (FY21-22)

Publications

1. Bergstrom, H. K.; Fong, K. D.; McCloskey, B. D. "Interfacial effects on transport coefficient measurements in Li-ion battery electrolytes." ***Journal of the Electrochemical Society*** (2021) 168, 060543.
2. Self, J.; Bergstrom, H. K.; Fong, K. D.; McCloskey, B. D. "A theoretical model for computing freezing point depression of Li-ion battery electrolytes." Journal of Electrochemical Society (2021) 168, 120532.

Presentations

1. "Ion correlations and transference numbers in polyelectrolyte solutions for Li-ion batteries." Padden Award Finalist Symposium, American Physical Society, March 2022. (Oral, invited) Presented by Kara Fong.
2. "The Onsager Framework for Transport Phenomena in Electrolyte Solutions." Young Investigator Lecture Series, Electrochemical Society San Francisco Section, November 2021. (Oral, Invited) Presented by Kara Fong.
3. "Ion transport and ion correlations in non-aqueous polyelectrolyte solutions." American Institute of Chemical Engineers, Boston, MA, November 2021. (Oral) Presented by Helen Bergstrom.
4. "Bridging Length Scales in Electrolyte Transport Theory via the Onsager Framework." Lennard-Jones Centre, University of Cambridge, November 2021. (Oral, Invited) Presented by Kara Fong.
5. Bridging Length Scales in Electrolyte Transport Theory via the Onsager Framework." American Institute of Chemical Engineers, Boston, MA, November 2021. (Oral) Presented by Kara Fong.
6. "Understanding Electrochemical Systems across Length and Time Scales." American Institute of Chemical Engineers, Boston, MA, November 2021. (Poster) Presented by Kara Fong.
7. "The Onsager Framework for Transport Phenomena in Electrolyte Solutions." Stanford University, August 2021. (Oral, Invited) Presented by Kara Fong.
8. "The Onsager Framework for Transport Phenomena in Electrolyte Solutions." Drexel University, July 2021. (Oral, Invited) Presented by Kara Fong.
9. "The Onsager Framework for Transport Phenomena in Electrolyte Solutions." University of Cambridge, May 2021. (Oral, Invited) Presented by Kara Fong.

Response to previous year's reviewer's comments

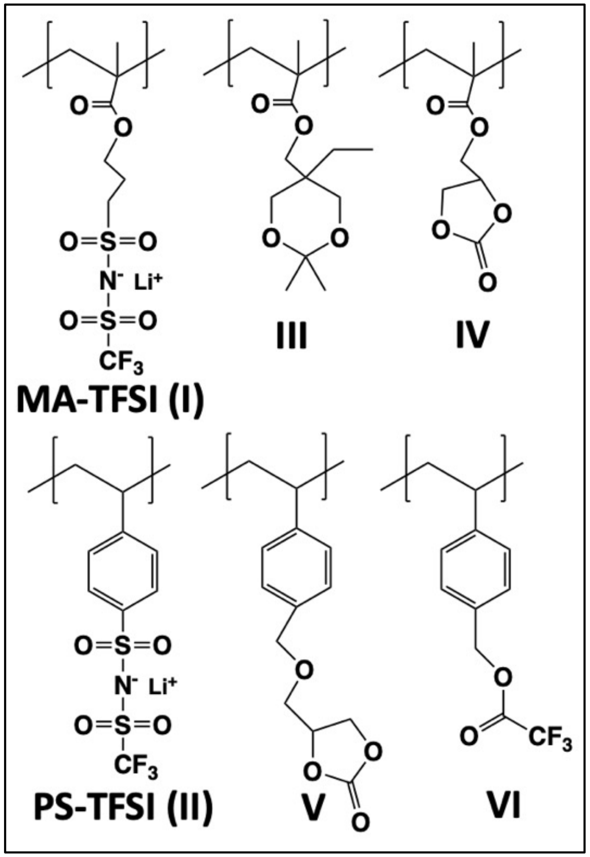
- Project was not reviewed last year.

Summary

- Demonstrated critical flaws in the standard (Nernst-Einstein) assumptions used to analyze polyelectrolyte transport
- For high conductivity liquid electrolytes that form high impedance Li metal interfaces, polarization techniques measure artefacts associated with the high impedance interface
  - Results in current ratios (ρ_+) that are correlated to the interfacial resistance, making ρ_+ not solely related to electrolyte transport.
- eNMR was developed to study ion velocities through an electric field in polyelectrolyte solutions
- Polyelectrolyte solutions were found to have low transference numbers due to strong coupling between anions.
- Developed Onsager transport theory and applied it to a coarse-grained molecular dynamics simulation model to guide polyelectrolyte design.

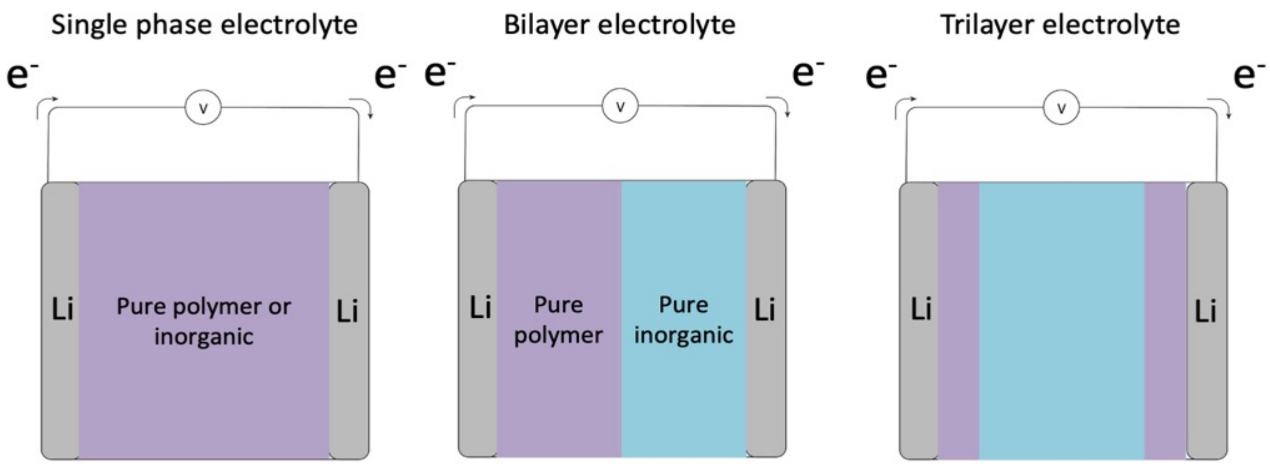
Future work: Polymer-inorganic composite electrolytes: Questions to answer and our strategy (I)

- Polymer matrix design?
  - Adhesion, film formation, ion conduction
  - Minor quantities of liquid solvent?
- Strategy
  - RAFT copolymerization
  - Characterize filming forming properties cast out of solvent or hot pressed
    - Inclusion of Lisicon or LiLaZrO particles
  - Analyze ion transport of pure polymers using electrochemical techniques and electrophoretic NMR



Future work: Polymer-inorganic composite electrolytes: Questions to answer and our strategy (II)

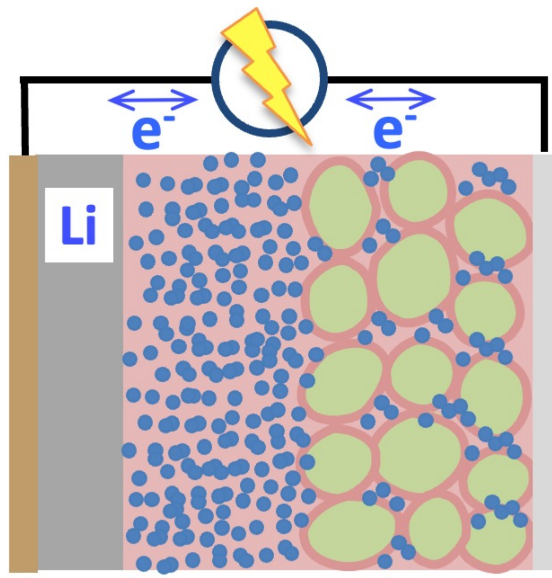
- How does ion transport occur in composites?
  - Do ions move easily across interfaces?
  - How does inorganic volume fraction impact ion transport?
- Strategy
  - Understand transport through well-defined geometries
  - NMR: isotopic labeling (^{6}Li vs ^{7}Li) and solid-state eNMR



Future work: Polymer-inorganic composite electrolytes: Questions to answer and our strategy (III)

- How do we design low resistance interfaces at the cathode?
  - Solid–solid contact resistance?
  - Reactivity with high voltage electrodes?

- Strategy
  - NMC coating
  - Differential electrochemical mass spectrometry, interfacial analysis developed in our lab for cathode reactivity
  - Tomography to understand particle distributions



Project targets:
- 25 μm thickness electrolyte
- >1 mS/cm conductivity @ 25 °C
- 70 vol% NMC in cathode
- 25 mg_{NMC}/cm^2

= LATP, LLZTO, LPS powder
= LATP coated NMC811
= anionic polymer matrix

Remaining challenges and barriers

- Li metal interfacial impedance. How do we design materials that remain stable against lithium, with interfaces that have good room temperature conductivity?
- Processability of inorganic thin films is challenging, particularly at the requisite low cost needed for electrolytes (~$5/m^2)
  - Will develop composites to impart polymer-like processability, while still taking advantage of the high conductivity of inorganic materials.
- Designing a porous cathode in a solid-state battery
  - Solid-solid contact resistance needs to be controlled
  - Ion conductive (compliant) polymer binders need to be designed